

ΠΡΑΚΤΙΚΑ ΤΗΣ ΑΚΑΔΗΜΙΑΣ ΑΘΗΝΩΝ

ΣΥΝΕΔΡΙΑ ΤΗΣ 14^{ΗΣ} ΙΟΥΝΙΟΥ 1956

ΠΡΟΕΔΡΙΑ ΚΩΝΣΤ. ΡΩΜΑΙΟΥ

ΠΡΑΞΕΙΣ ΚΑΙ ΑΠΟΦΑΣΕΙΣ ΤΗΣ ΑΚΑΔΗΜΙΑΣ

ΚΛΗΡΟΔΟΤΗΜΑ ΙΩΑΝΝ. ΜΑΤΡΑΓΚΑ

Ἡ Ἀκαδημία ἀπεδέχθη τὸ ἐκ 2 ἀκινήτων κληροδότημα τοῦ ἐν Ἀθήναις ἀποβιώσαντος Σωτηρίου Ἰωάννου Ματράγκα, διὰ τῆς ἀπὸ 24 Αὐγούστου 1955 ἰδιογράφου διαθήκης του, δημοσιευθείσης ὑπὸ τοῦ Πρωτοδικείου Ἀθηνῶν τῆ 16ῃ Μαΐου 1956, συνταχθέντος τοῦ σχετικοῦ ὑπ' ἀριθ. 1984 πρακτικοῦ.

Ἐκ τῶν προσόδων τοῦ κληροδοτήματος τούτου ἡ Ἀκαδημία θὰ προκηρύσσει ἀργότερον κατ' ἔτος βραβεῖον εἰς μνήμην Ἀλεξάνδρου καὶ Σωτηρίου Ἰ. Ματράγκα διὰ τὴν καλυτέραν ἔκδοσιν λυρικῶν ποιημάτων.

ΨΗΦΙΣΙΣ ΤΟΥ ΠΡΟΫΠΟΛΟΓΙΣΜΟΥ 1956 (Γ' Ἐξαμ.).

Ψηφίζεται ὁ προϋπολογισμὸς τῶν ἐσόδων καὶ ἐξόδων τῆς Γ' ἔξαμηνίας τοῦ οἰκονομικοῦ ἔτους 1955 - 56, ἧτοι ἀπὸ 1ης Ἰουλίου μέχρι 31 Δεκεμβρίου 1956.

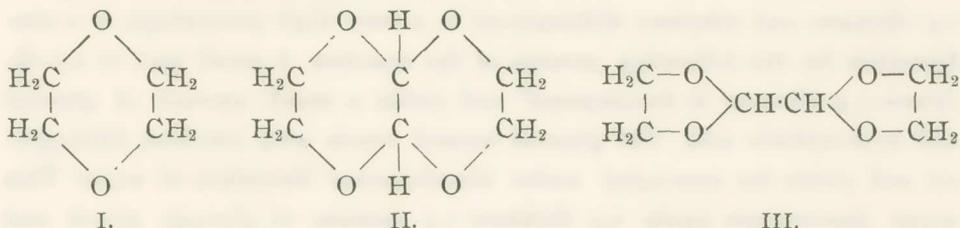
ΑΝΑΚΟΙΝΩΣΕΙΣ ΜΗ ΜΕΛΩΝ

ΟΡΓΑΝΙΚΗ ΧΗΜΕΙΑ.— On some acetals of glyoxal, by George Tsatsaronis*. Ἀνεκοινώθη ὑπὸ τοῦ κ. Κωνστ. Βέη.

The acetals of glyoxal are prepared from three-molecular glyoxal with alcohol and hydrochloric acid or from glyoxal sulfate and alcohol. In earlier works it was proved that 2,3-dichloro-1,4-dioxane¹ (I) is decomposed by water to glyoxal, glycol and hydrochloric acid. By heating 2,3-di-

* ΓΕΩΡΓΙΟΥ ΤΣΑΤΣΑΡΩΝΗ, Περὶ ἀκεταλῶν τῆς γλυοξάλης.

chloro-1,4-dioxane with glycol two isomers² are obtained, which, by further investigation of their structure, proved to be cyclic acetals of glyoxal, namely naphthodioxane (II) and bis-(1,3-dioxolane)-2,2' (III). On the other hand, these substances had been prepared by W. Baker and F. B. Field³ from glyoxal sulphate and ethylene glycol, and by L. Donciu⁴ from glyoxal, glycol and gaseous hydrochloric acid.



The formation of these substances from 2,3-dichloro-1,4-dioxane and particularly that of bis-(1,3-dioxolane)-2,2' (III), makes it necessary to accept, that it is preceded by a decomposition of 2,3-dichloro-1,4-dioxane to glyoxal, glycol and hydrochloric acid, because otherwise the formation of bis-(1,3-dioxolane)-2,2 (III) would be impossible.

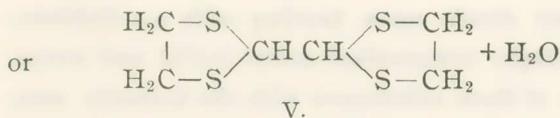
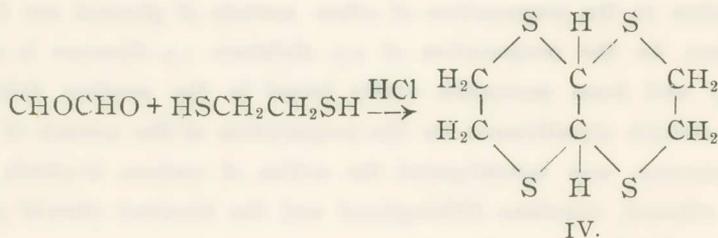
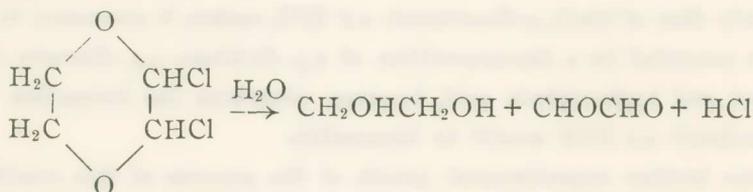
Some further experimental proofs of the process of this reaction and its application to the preparation of other acetals of glyoxal are described in this paper. As the preparation of 2,3-dichloro-1,4-dioxane is comparatively easy and from materials easily found in the market, this method takes up a certain significance for the preparation of the acetals of glyoxal. For this purpose was investigated the action of various alcohols, namely, methanol, ethanol, ethylene dithioglycol and the bivalent phenol pyrocatechine, on 2,3-dichloro-1,4-dioxane.

Methanol and ethanol react slowly upon heating with 2,3-dichloro-1,4-dioxane yielding correspondingly tetramethyl-acetal (10%) and tetraethyl-acetal (20%). The identity of these substances with the formerly mentioned acetals has been ascertained by means of the boiling point and the formation of the phenylozazone of glyoxal.

Ethylene dithioglycol reacts slowly upon heating with 2,3-dichloro-1,4-dioxane and yields a crystalline substance (71%), under simultaneous evolution of gaseous hydrochlorid acid. Quantitative analysis of this substance gives results corresponding to the formula $C_6H_{10}S_4$. Further, it was identified as bis-ethylene mercaptal of glyoxal, which was prepared by Fasbender⁵ by passing gaseous hydrochloric acid over a mixture of glyoxal

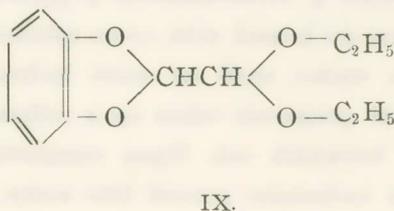
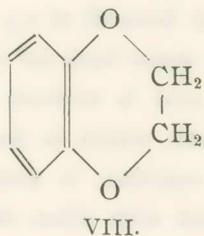
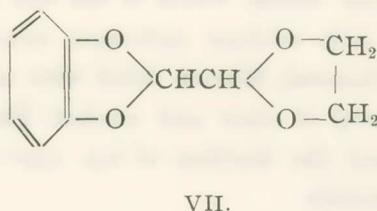
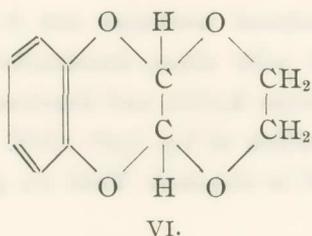
and ethylene dithioglycol. The identification was effected by quantitative analysis, by measuring the melting point of the substance and that of a mixture with original bis-ethylene mercaptal of glyoxal and, at last, by comparing the X-ray Powder Diagrams of the preparate and original bis-ethylene mercaptal of glyoxal.

This synthesis of bis-ethylenemercaptal of glyoxal from 2,3-dichloro-1,4-dioxane and ethylene dithioglycol in a very high percentage, is a confirmation for the following process of the reaction. A small part of 2,3-dichloro-1,4-dioxane is decomposed⁶ and yields a small amount of glyoxal and hydrochloric acid. The glyoxal formed reacts with ethylene dithioglycol and yields the mercaptal under simultaneous liberation of water. This water decomposes again 2,3-dichloro-1,4-dioxane to glyoxal, glycol and hydrochloric acid.



It has not been ascertained to which of these two formulae IV and V corresponds our preparate.

The action of pyrocatechine upon 2,3-dichloro-1,4-dioxane results in a vivid reaction and the formation of a crystalline substance of acetalic odour, which with sulfuric acid yields a reddishviolet colour. Quantitative analysis of this substance gives the empirical formula $\text{C}_{10}\text{H}_{10}\text{O}_4$, which is in agreement with the substances of formulae VI and VII.



Substance VI can be named [(pyrocatechine- $1,2$)-(glycol- $1,2$)]-diacetal of glyoxal or else benzonaphthodioxane. In the same way, substance VII can be named [(pyrocatechine- $1,1$)-(glycol- $2,2$)]-diacetal of glyoxal.

Of the two formulae VII is most probably the one corresponding to the preparate. In favour of it we have the following: (a) The above said about the decomposition of 2,3-dichloro-1,4-dioxane and the formation of acetals when we act with alcohols upon the products of the decomposition (a fact that permits the formation either of VI or VII). (b) The reddishviolet colour given by the preparate when acted upon with sulfuric acid. It is known that derivatives of pyrocatechine of the formula IX, which resembles formula VII, give with sulfuric acid a reddishviolet colour⁷. On the other hand, in a paper of ours to be published shortly, it is stated that benzodioxene VIII, which resembles VI, gives with sulfuric acid a blue colour. Consequently formula VII is in accord with the colour given by the preparate with sulfuric acid. (c) The low melting point of the substance, 75°C, as compared with that of naphthodioxane (11) 136°C. This is one further indication that the preparate has not the structure of naphthodioxane VI.

Experimental part.

Preparation of tetramethylacetal of glyoxal: 6.3 gr. (0.04M) of 2,3-dichloro-1,4-dioxane are heated with 12 c.c. methanol over a water bath until no more hydrochloric acid is evolved. This reaction is very slow, 20-25 hours being required for its completion. At the beginning the preparate takes up

a yellowish colour, which in the end is rendered brownish red. It is neutralized with calcium carbonate, extracted with ether, decolourized with animal charcoal, filtered, dried with anhydrous K_2CO_3 and fractioned after the removal of ether and alcohol. The fraction of b.p. $150^\circ-170^\circ C$ is redistilled and the fraction of b.p. $159^\circ-162^\circ C$ is obtained. Yield 0.5 gr. 10% approximately.

Preparation of tetraethylacetal of glyoxal: 6.3 gr. (0.04 M) of 2,3-dichloro-1,4-dioxane are heated with 12 c.c. ethanol over a water bath for 10 hours with a reflux cooler, until no more hydrochloric acid is evolved. At the beginning the prepate takes up a yellowish colour, which in the end is rendered to brownish red. Upon completion the reaction, is neutralized with calcium carbonate, poured into water, extracted with ether, the ether solution washed up with water, decolorized with animal charcoal, filtered and dried with $CaCl_2$, the ether let to evaporize and in the end there remains a brownish red oil. Upon distillation this oil is separated into two fractions, one up to $190^\circ C$ and another between 190° and $205^\circ C$. The two fractions are distilled separately and a fraction $200^\circ-203^\circ C$ is obtained in an amount of 0.8 gr. Yield 20% approximately.

Preparation of phenylozazone of glyoxal: 0.2 gr. of tetramethyl- or tetraethylacetal of glyoxal are heated with a few drops of hydrochloric acid for a few minutes, then neutralized. 0.2 gr of phenylhydrazine dissolved in acetic acid are added. Yellow needles separate of m.p. $182^\circ C$. M.p. of the ozazone of glyoxal $179^\circ-180^\circ C$.

Preparation of diethylene mercaptal of glyoxal: To 5 gr (0.053 M) ethylene dithioglycol are added 8,5 gr. (0.053 M) 2,3-dichloro-1,4-dioxane and heated over a water bath. With the commencement of the reaction begins evolution of hydrochloric acid, which ends after 8 hours. After cooling the prepate crystallizes, then it is filtered in vacuo and the filtrate heated for an hour. From this is obtained an additional small amount of the crystalline substance. The substance is recrystallized from alcohol or a mixture of benzene and petroleum ether. Yield 4 gr 71%. M.p. $133^\circ C$.

Analysis: For $(C_{10}H_{10}S_4)$ calc. C 34.71% H 4.79% S 60.87%
 found C 34.48% H 4.93% S 60.73%

Preparation of [(pyrocatechino-1,1)-(glycol-2,2)]-diacetal of glyoxal: 2.2 gr (0.02 M) of pyrocatechine and 3.1 gr (0.02 M) of 2,3-dichloro-1,4-dioxane are heated over a water bath. At the beginning a vivid reaction

takes places and that is why is cooled externally by means of water. Heating is continued until no more hydrochloric acid is evolved. Then alkali is added until it is rendered strogly alkaline and distilled with vapour. 1.3 gr of a white crystalline substance are obtained which then is filtered and recrystallized from alcohol. M.p. 75°C. With sulfuric acid it gives reddish violet colour.

Analysis: for (C₁₀H₁₀O₄) calc. C 61.83 % H 5.19 %
found C 62.07 % H 5.22 %

The same substance is obtained if toluene or benzene is used as solvent, to reduce the concentration of pyrocatechine and 2,3-dichloro-1,4-dioxane. In this way the reaction is rendered milder.

Π Ε Ρ Ι Δ Η Ψ Ι Σ

Εἰς τὴν παροῦσαν ἐργασίαν περιγράφονται πειράματα ἀποδείξεως τοῦ χημισμοῦ τῆς ἀντιδράσεως ἀλκοολῶν μετὰ τοῦ 2,3-δὶχλωρο-1,4-διοξανίου I καὶ ἡ παρασκευὴ μερικῶν ἀκεταλῶν τῆς γλυοξάλης. Κατὰ τὴν ἐπίδρασιν ἀλκοολῶν παρουσίᾳ ἐλαχίστης ποσότητος ὕδατος ἐπὶ τοῦ 2,3-δὶχλωρο-1,4-διοξανίου σχηματίζονται γλυοξάλη, ὕδροχλώριον καὶ γλυκόλη. Ἡ σχηματιζομένη γλυοξάλη παρουσίᾳ τοῦ ὕδροχλωρίου ἀντιδρᾷ μετὰ τῶν ἀλκοολῶν ὅποτε λαμβάνονται ἀκετάλαι τῆς γλυοξάλης.

Ἡ μεθανόλη καὶ ἡ αἰθανόλη ἀντιδροῦν μετὰ τοῦ I σχηματίζουσαι ἀντιστοιχῶς τὰς τετραμέθυλο-καὶ τετρααἰθυλο-ἀκετάλας τῆς γλυοξάλης. Ἡ αἰθυλένοδιθειο-γλυκόλη παρέχει τὴν δισαιθυλένομερκαπτάλην τῆς γλυοξάλης IV ἢ V καὶ ἡ πυροκατεχίνη νέαν ἀκετάλην τὴν (πυροκατεχίνο-1,1)-(γλυκολο-2,2)-διακετάλην τῆς γλυοξάλης VII.

Ἐπειδὴ αἱ ἀποδόσεις τῶν ἀκεταλῶν εἶναι ἱκανοποιητικαὶ καὶ αἱ πρῶται ὕλαι παρασκευάζονται εὐκόλως ἐξ ὑλῶν τοῦ ἐμπορίου, ἡ μέθοδος αὕτη ἀποκτᾷ σημασίαν προκειμένου περὶ τῆς παρασκευῆς τῶν ἀκεταλῶν τῆς γλυοξάλης.

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